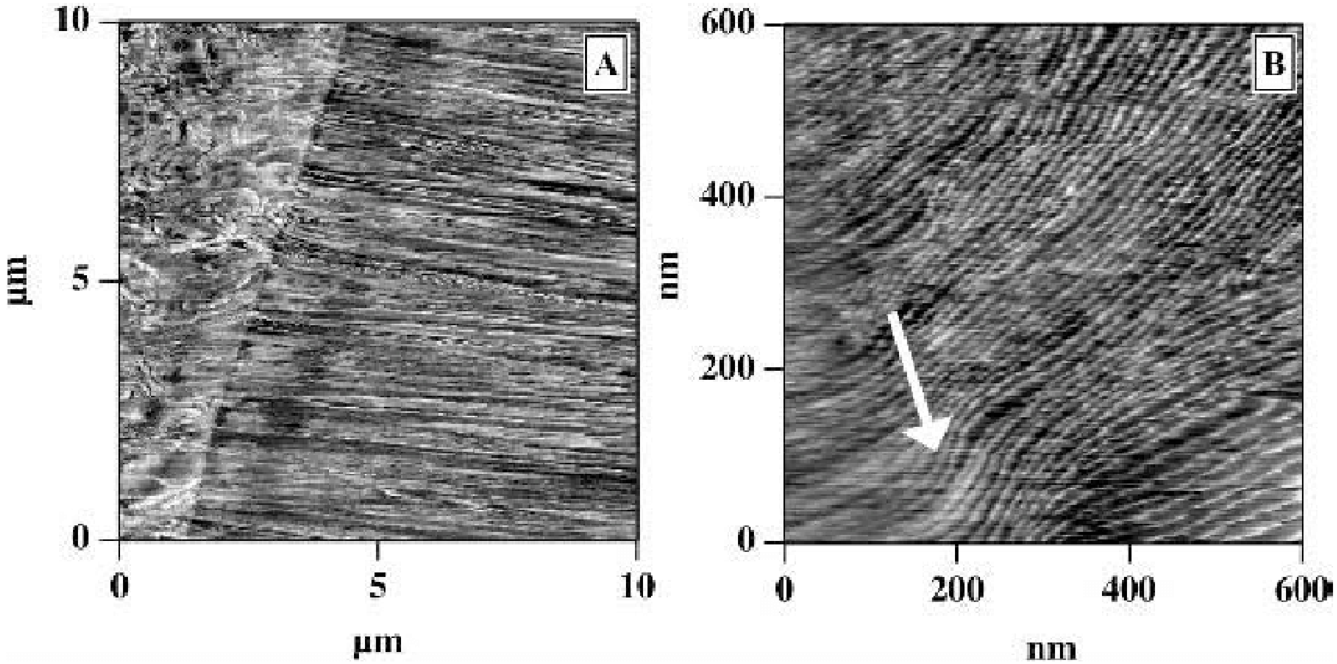
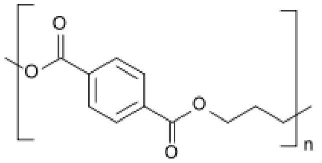
The Crystalline State



High temperature AFM images of the semicrystalline structure of PTT (Poly(trimethylene terephthalate): crystallization and imaging at 210°C. Structure of a spherulitic band, as observed at the micrometer (A) and sub-micrometer (B) scales. The arrow indicates the onset of a concerted lamellar twist involving many crystals



Dimitri A. Ivanov,Sergei N. Magonov
Atomic Force Microscopy Studies of Semicrystalline Polymers at Variable Temperature,
Polymer Crystallization: Observations, Concepts and Interpretations (pp.98-130)
Springer-Verlag Berlin Heidelberg 2003

Introduction

- Synthetic polymers like PE, isotactic polypropylene, Nylon 6,6 and Teflon can crystallize and account for the majority of worldwide annual production.

- Crystallinity conveys enhanced mechanical strength, greater resistance to degradation and better barrier properties.

- Crystalline Polymers are never totally crystalline because of their long-chain nature and subsequent entanglements → semi-crystalline polymers

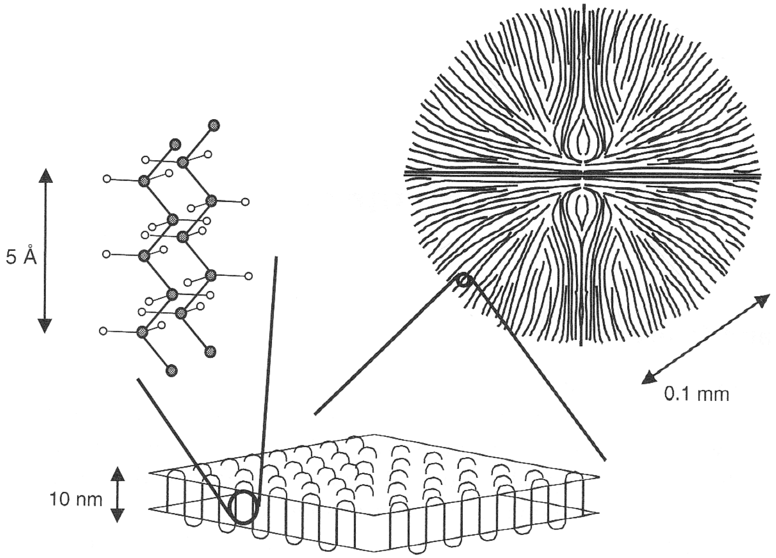


Figure 13.1 Three levels of structure in a crystalline polymer. The packing of individual helical chains gives unit cells with dimensions of a few angstroms. The unit cells are packed into chain-folded lamellae, with characteristic thicknesses on the order of 10 nm. The lamellae splay, bend, and branch to form spherulites, which can exceed millimeters in size. The space between the individual lamellae is filled with amorphous material.

Outline

The Crystalline Phase: Requirements and Characterization

Degree of Crystallinity

Model of semi-crystalline Polymers and their amorphous fractions

Thermodynamic of Crystallization

Dependence of T_m on
- Chemical Structure
- Lamellae Thickness
- Molecular Weight

Kinetic of Crystallization: Nucleation and Growth

Kinetic of Bulk Crystallization: Avrami Model

Fibers

The Crystalline Phase: Why polymers crystallize?

Requirement: Regularity of structure in the polymer

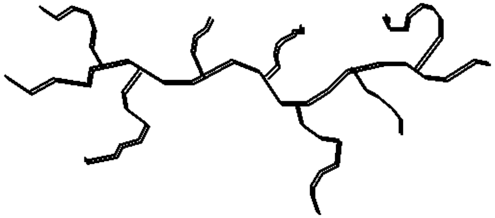
1. Defined microstructure

   -Statistical/random copolymers are generally amorphous.

   -Block copolymers containing crystalline blocks can undergo crystallization

2. Little or no branching

   Branching generally decreases the tendency towards crystallization



The Crystalline Phase: Why polymers crystallize?

3. Polymer stereochemistry

Isotactic and syndiotactic polymers usually crystallize, whereas atactic polymers do not

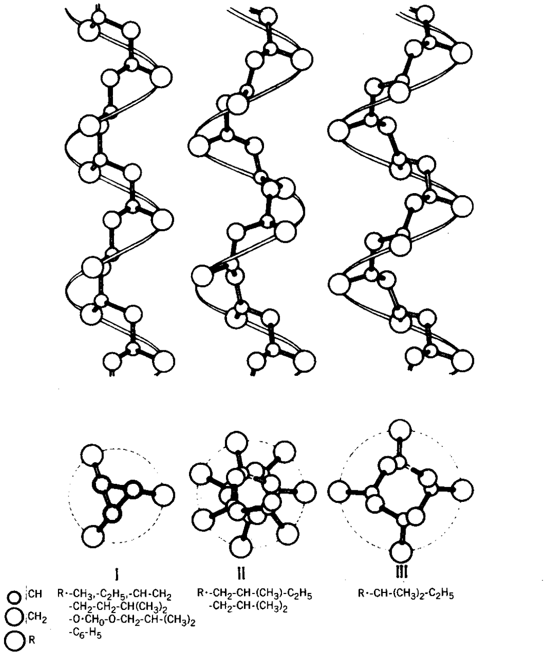
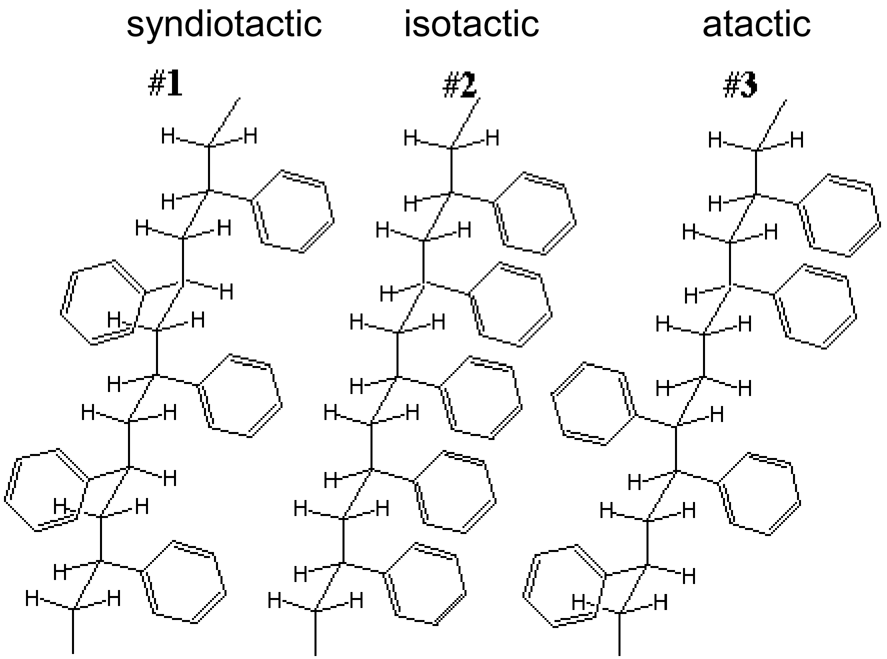


FIGURE 5.14 Possible types of helices for isotactic chains, with various lateral groups (68).

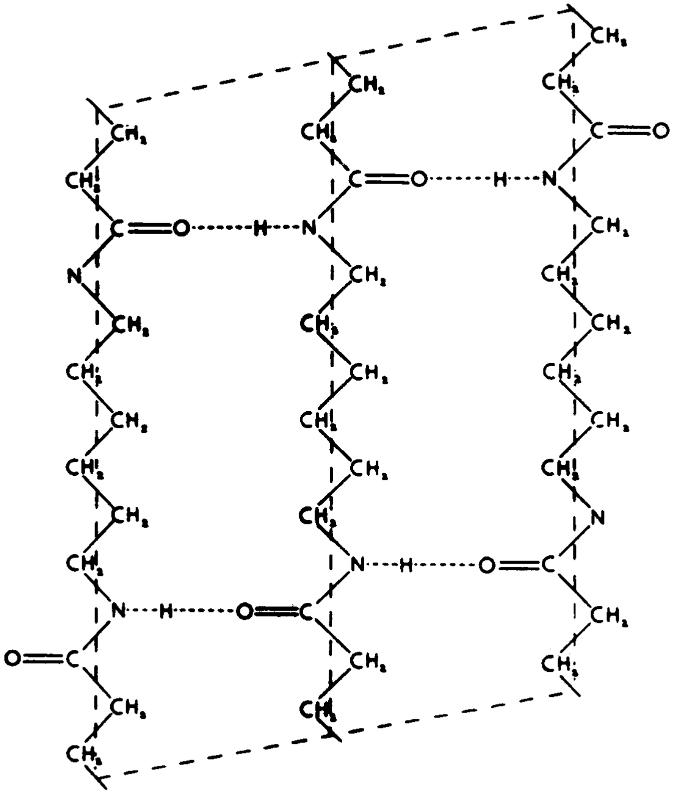
Tacticity of polystyrene



The Crystalline Phase: Why polymers crystallize?

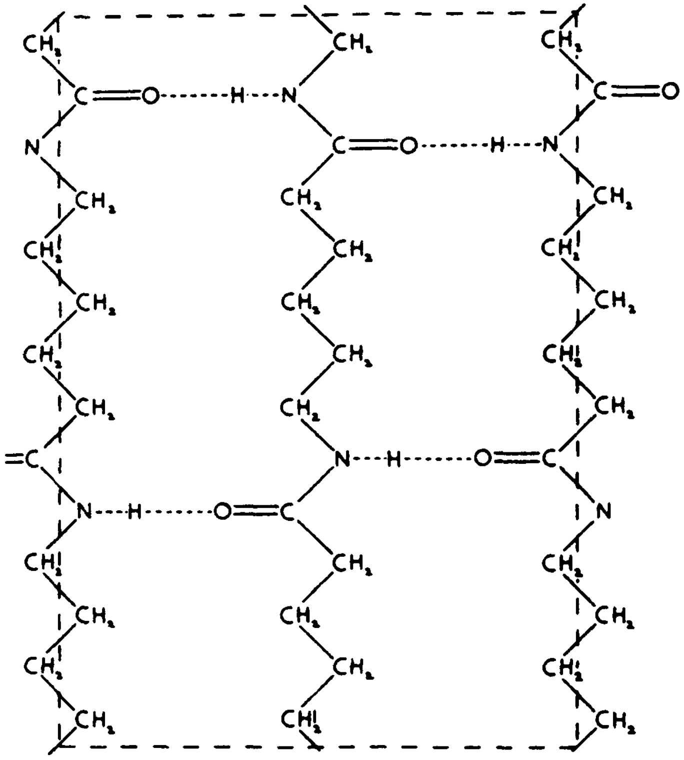
4. Importance of intermolecular interactions

Polar groups that can give rise to intermolecular interactions



(a)

FIGURE 5.16 The hydrogen-bonded structure of two polyamides (nylons). The unit cell face is shown dotted. (*a*) Nylon 6, 6; (*b*) nylon 6 (69).

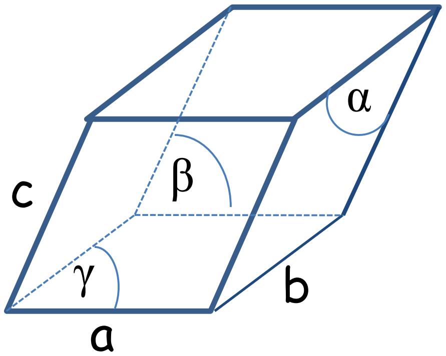


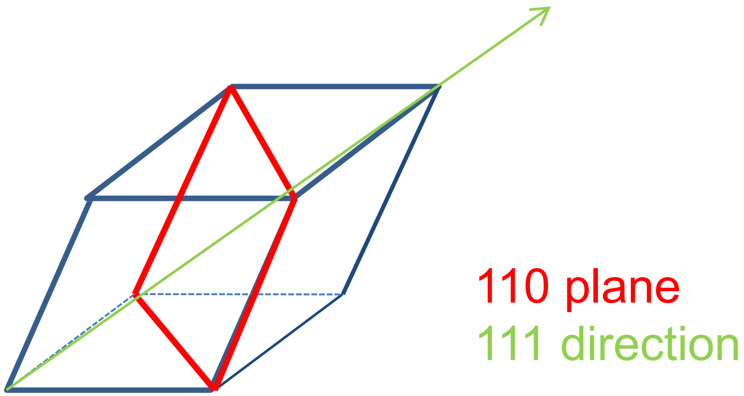
(*b*)

FIGURE 5.16 (*Continued*)

Characterization of the Crystalline Phase

Unit cell = smallest level of structure displayed by polymer crystals, contains the smallest number of atoms





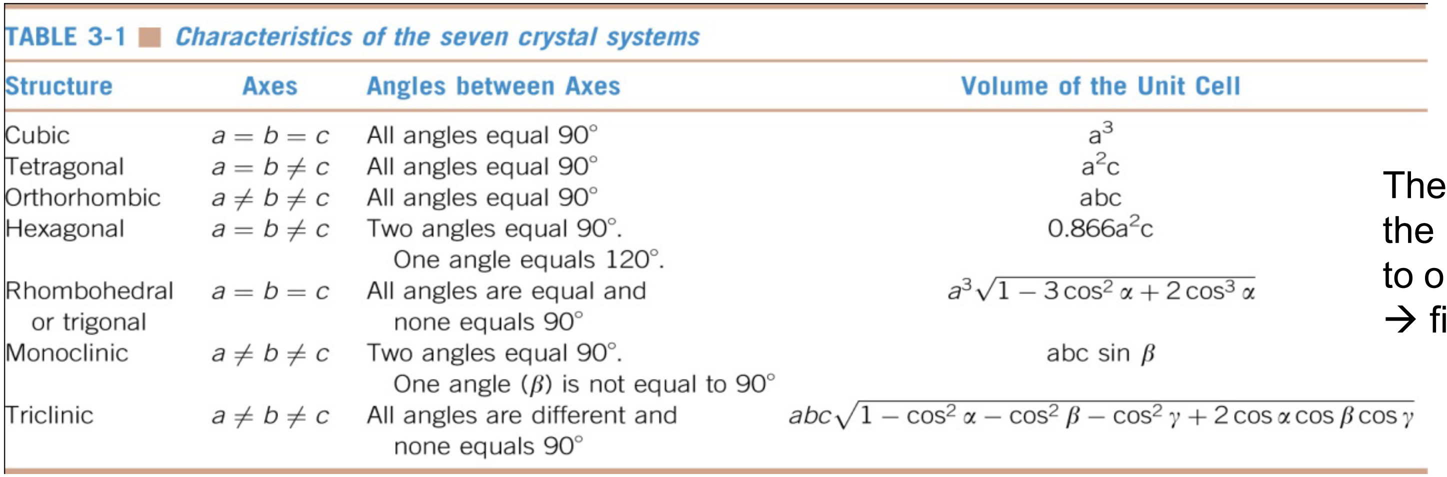


TABLE 3-1 ▨ ***Characteristics of the seven crystal systems***

Structure	Axes	Angles between Axes	Volume of the Unit Cell
Cubic	$a = b = c$	All angles equal 90°	a^3
Tetragonal	$a = b \neq c$	All angles equal 90°	a^2c
Orthorhombic	$a \neq b \neq c$	All angles equal 90°	abc
Hexagonal	$a = b \neq c$	Two angles equal 90°. One angle equals 120°.	$0.866a^2c$
Rhombohedral or trigonal	$a = b = c$	All angles are equal and none equals 90°	$a^3\sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha}$
Monoclinic	$a \neq b \neq c$	Two angles equal 90°. One angle (β) is not equal to 90°	abc sin β
Triclinic	$a \neq b \neq c$	All angles are different and none equals 90°	$abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$

The overall direction of the backbone corresponds to one axis of the unit cell
→ fiber axis (c-axis)

X-ray Diffraction

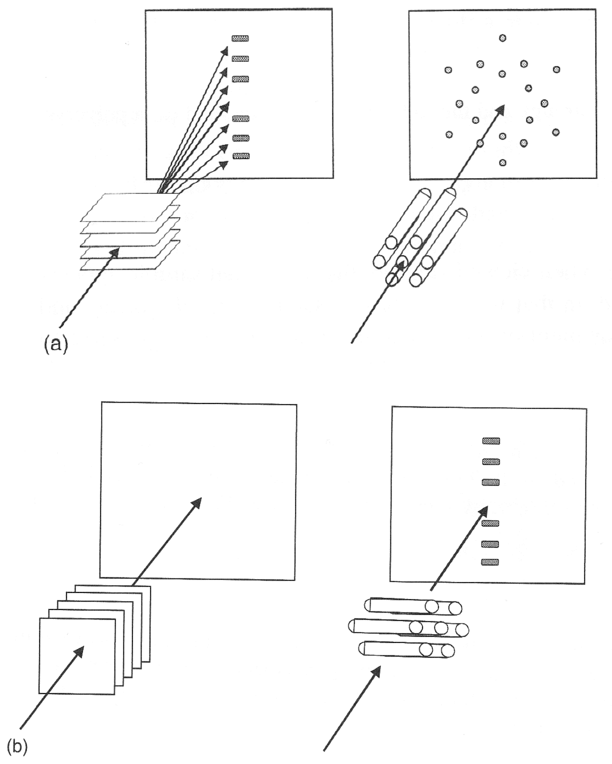
Bragg's Law $$d = \frac{n\lambda}{2\,sin\theta}$$

d: distance between successive identical planes of atoms in the crystal

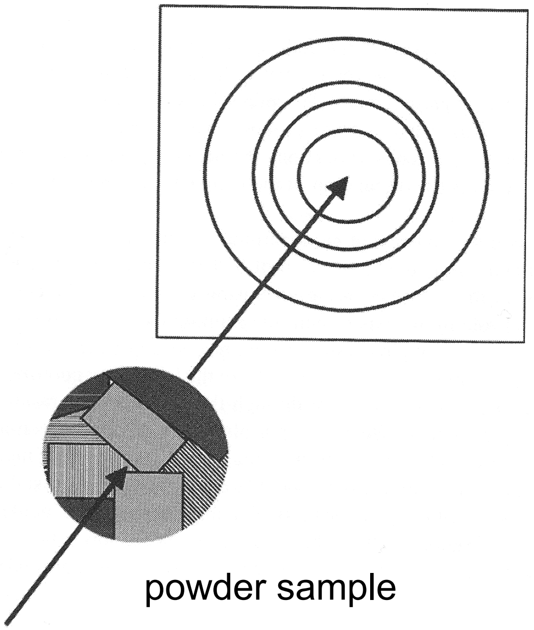
λ : X-ray wavelength

θ: angle between x-ray beam and these atomic planes

n: order of diffraction



single crystal



powder sample

Examples of Crystal Structures

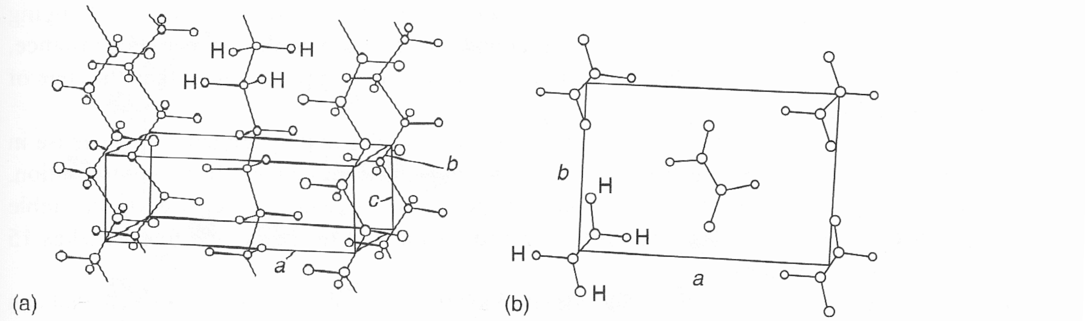


Figure 13.5 Crystal structure of polyethylene: (a) unit cell shown in relationship to chains and (b) view of unit cell perpendicular to the chain axis. (Reprinted from Bunn, C.W., *Fibers from Synthetic Polymers*, R. Hill (Ed.), Elsevier, Amsterdam, 1953. With permission.)

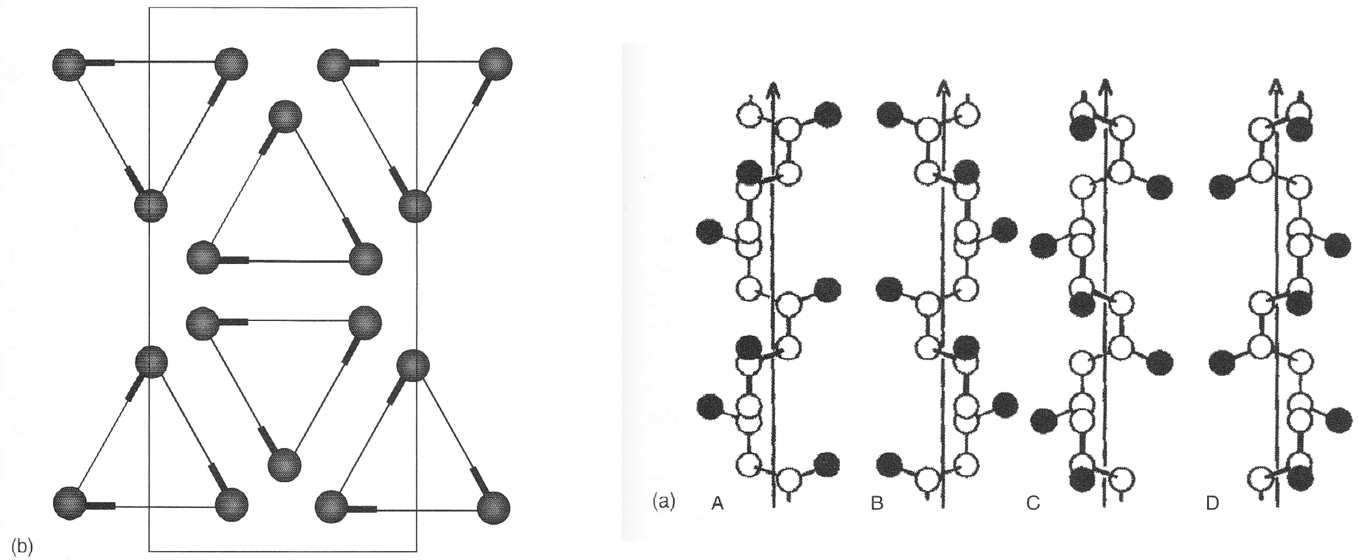


Figure 13.7 (a) Illustration of four possible 3/1 helices for an isotactic vinyl polymer such as polypropylene. A and D are right-handed, B and C are left-handed, A and D are equivalent if inverted, as are B and C. (Reprinted from Wunderlich, B., *Macromolecular Physics, Vol. I: Crystal Structure, Morphology, Defects*, Academic Press, New York, 1973. With permission.) (b) The polypropylene unit cell looking down the chain axis. Each apex of a triangle indicates a methyl group. The thick line segments suggest the projection of the bond to the methyl group; there are three left-handed and three right-handed helices shown.

Degree of Crystallinity

The degree of crystallinity of a semi-crystalline polymer can be defined in two ways:

- **By Volume**

$$\boxed{X_c^v = \frac{\rho - \rho_a}{\rho_c - \rho_a}}$$

ρ : density of the semi-crystalline polymer
ρ_c : density of the crystalline phase
ρ_a : density of the amorphous phase

- **By Mass**

$$\boxed{X_c^w = \frac{V_{sp} - V_{sp,a}}{V_{sp,c} - V_{sp,a}}}$$

V_{sp} : specific volume of the semi-crystalline polymer
$V_{sp,c}$: specific volume of the crystalline phase
$V_{sp,a}$: specific volume of the amorphous phase

These quantities are related to one another through the following equation

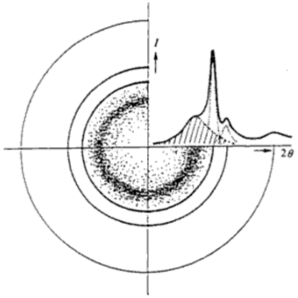
$$\boxed{X_c^w = \frac{\rho_c}{\rho_a} X_c^v}$$

Generally, the densities of the amorphous and crystalline phases are similar and so therefore are the degrees of crystallinity measured by mass and volume

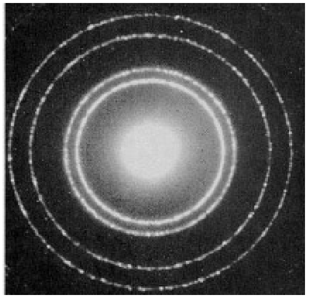
Methods for Measuring the Degree of Crystallinity

- (Density gradient columns (X_C^V and X_C^W)
  - Necessity for hypothetical 100% amorphous and 100% crystalline polymers)

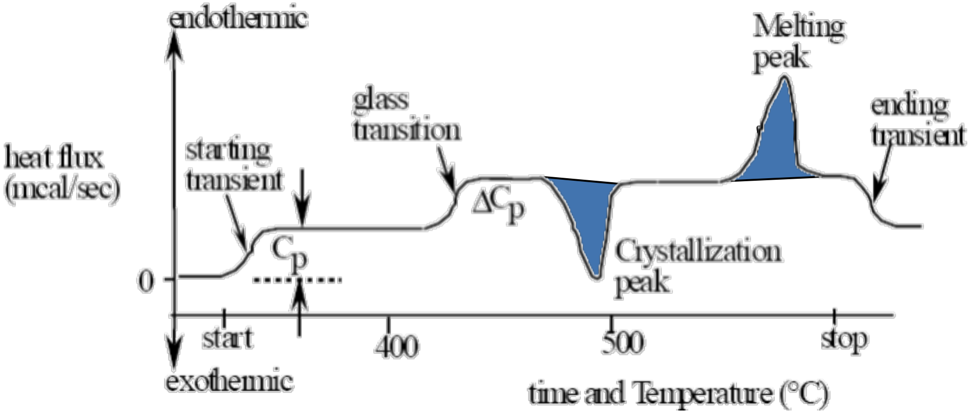
- X-ray diffraction (X_C^V)
  - Integration of the peaks from the amorphous and crystalline regions



Schematic illustration of an diffraction diagram of an unoriented crystalline polymer. Radial intensity distribution is given in the first quadrant (*cf.* Fig. 14.4).



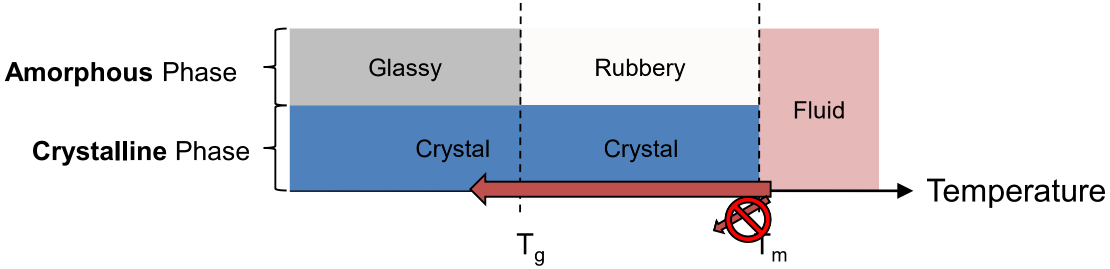
- Differential Scanning Calorimetry (DSC) (X_C^W)
  - The heat of formation or melting of the crystalline regions is directly proportional to its mass



Controlling the Degree of Crystallinity

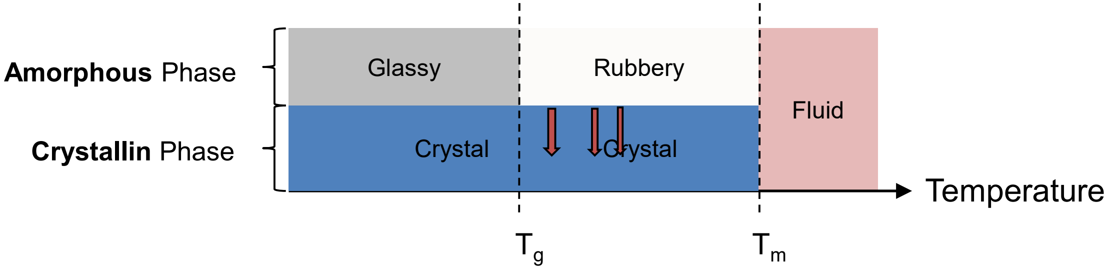
Quenching

- From the molten state, the polymer is rapidly cooled so that crystallization cannot occur.
- This is usually done in liquid nitrogen



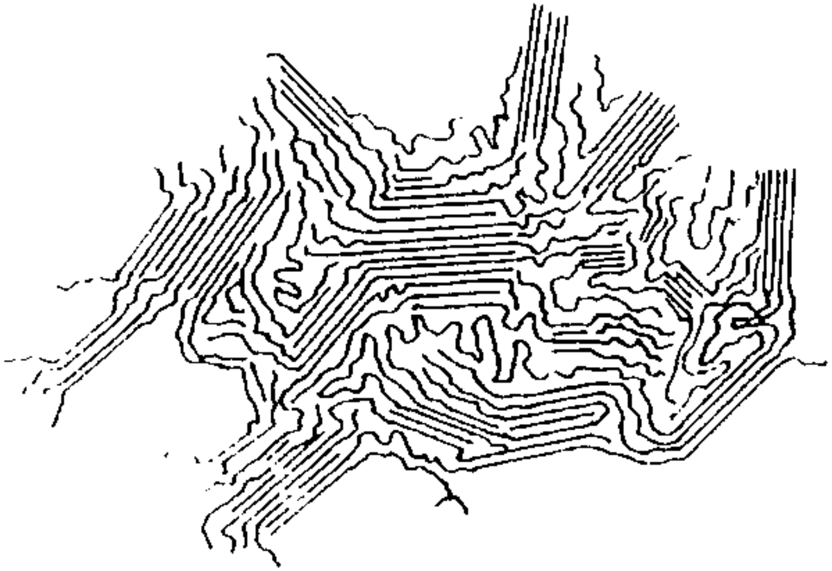
Annealing

- The polymer is maintained at elevated temperature so that the polymer chains have sufficient mobility to adopt a more thermodynamically favorable configuration (crystal)
- The most elevated temperature is T_m
- Annealing cannot be done below T_g



How do Polymer Chains Crystallize?

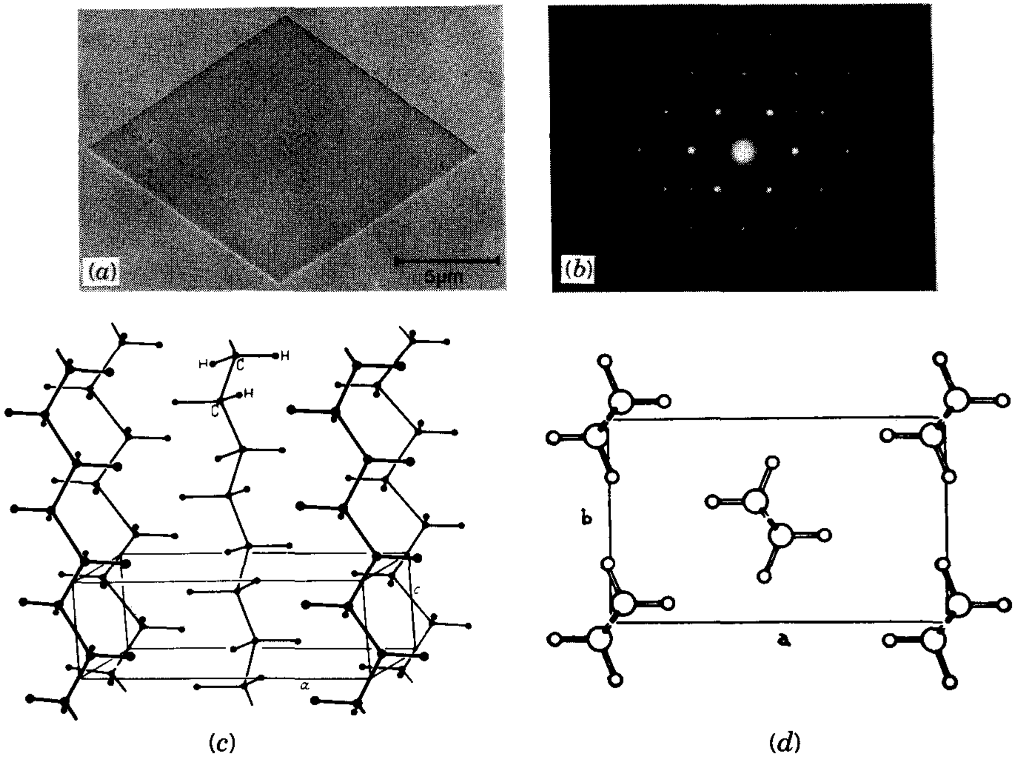
Early model: the fringed micelle model



Crystallites of about 100 Å length in an amorphous matrix. Above the T_g of the amorphous phase (and below the T_m of the crystalline phase), the crystallites act as physical crosslinks that prevent flow of the polymer chains, which explains the leathery behaviour of semi-crystalline polymers above their T_g.

Crystallization of Polymers from Dilute Solution

Crystallization of polymers from dilute solution can yield single crystals.
First example: A. Keller (1957), polyethylene



A study of polyethylene single-crystal structure. (a) A single crystal of polyethylene, precipitated from xylene, as seen by electron microscopy. (b) Electron diffraction of the same crystal, with identical orientation. (c) Perspective view of the unit cell of polyethylene, after Bunn. (d) View along C (chain axis). This latter corresponds to the crystal and diffractions orientations in (a) and (b). By courtesy of A. Keller and Sally Argon.

A. Keller, Phil. Mag. 2, 1957, 1171.

Problem: The contour length of the polyethylene is about 2000 Å;

The thickness of the crystals is 110 – 140 Å.

How do the polymer chains pack?

The New Model: the folded chain

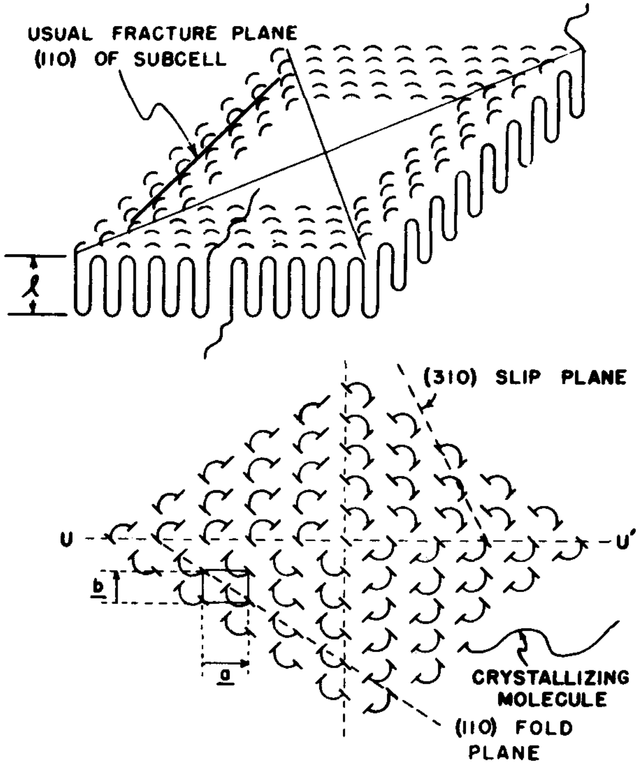
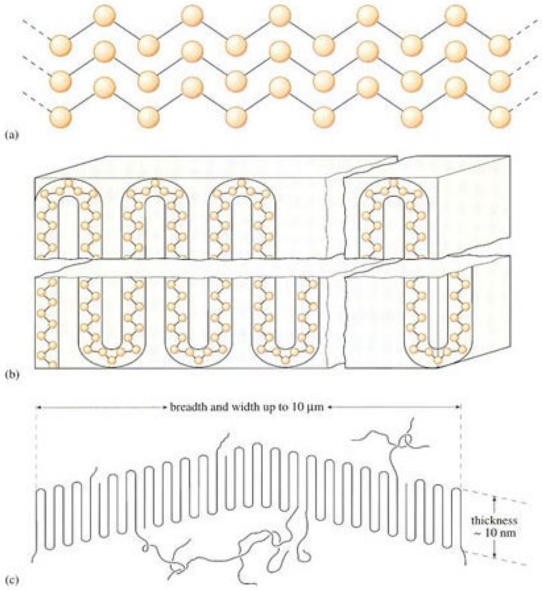
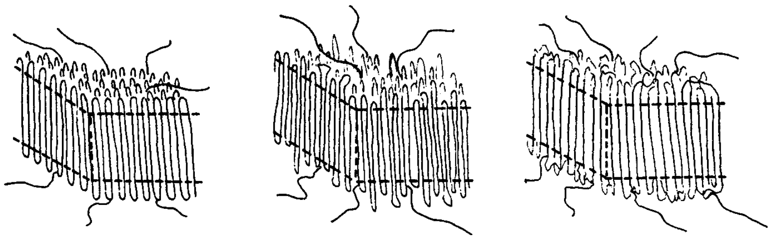


FIGURE 5.19 Schematic view of a polyethylene single crystal exhibiting adjacent reentry. The orthorhombic subcell with dimensions *a* and *b*, typical of many n-paraffins, is illustrated below (77).

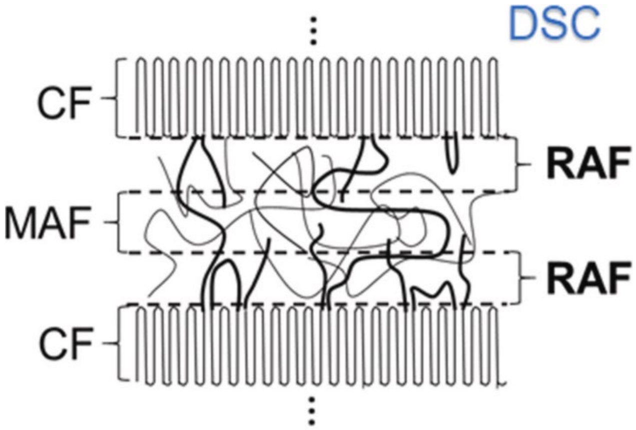


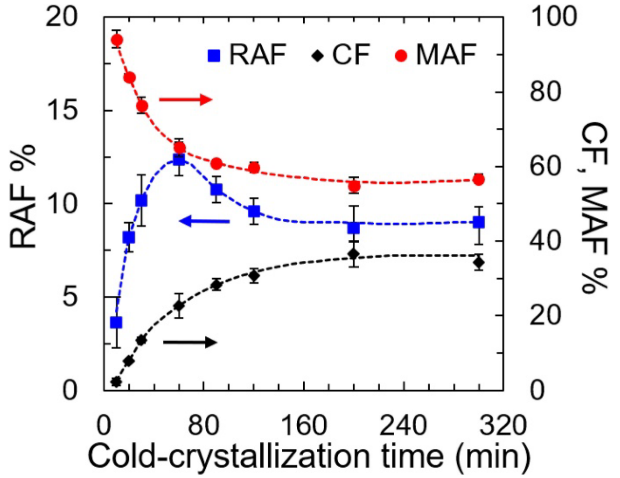


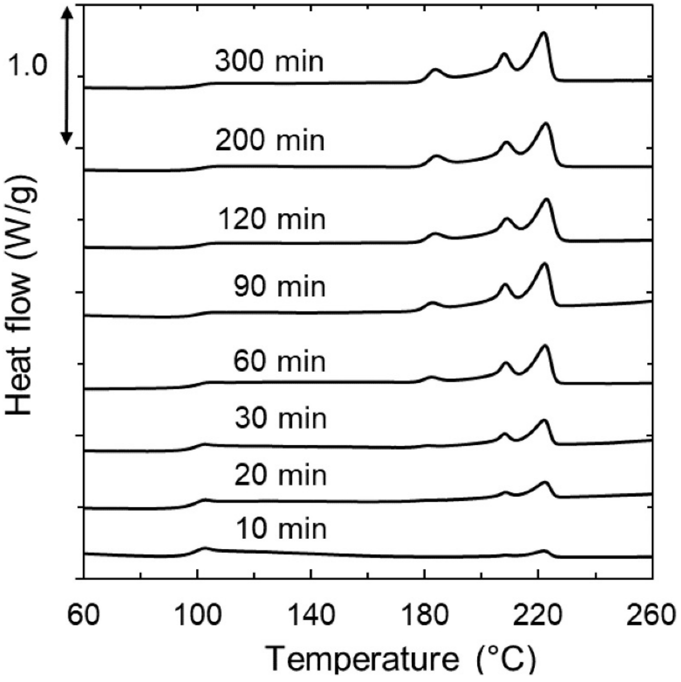
(a) (b) (c)

FIGURE 3.16. Folded-chain lamella model: (a) regular adjacent folds; (b) irregular adjacent folds; and (c) nonadjacent switchback.

The 3 –Phase Model: rigid and mobile amorphous fraction







DSC heat flow curves of bulk iPS samples cold-crystallized at 170 °C for various timeframes.

$$CF = \frac{\Delta H_{m,sc}}{\Delta H_{m,c}}$$

$\Delta H_{m,c}$ = 86.3 Jg^{-1}

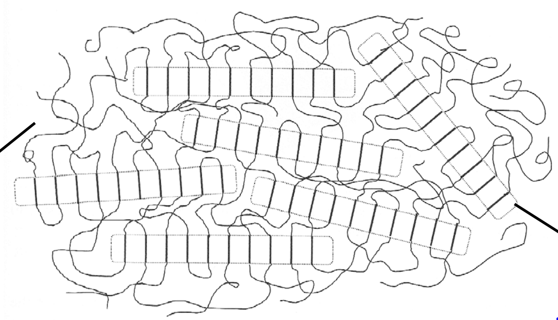
$$MAF = \frac{\Delta C_{p,M}}{\Delta C_{p,am}}$$

$\Delta C_{p,am}$ = 0.33 J(g°C)$^{-1}$

$$CF + MAF + RAF = 1$$

B. Chen, B. Feng, T. Wong, J.M. Torkelson;
J. Polym. Sci. 2023, 61, 2440-2450.

Thermodynamics of Crystallization



glass transition T_g

Melting T_m and Crystallization T_c
are thermodynamic 1st-order transitions

amorphous phase

a random jumble of
intertwined chains

crystalline phase

long sections of chains
fully extended and closely packed

once crystallizations starts
different sections of a chain
may be in several different
crystallites

↓

nonequilibrium mixture of
crystalline and amorphous
regions within the material

Thermodynamics of Crystallization

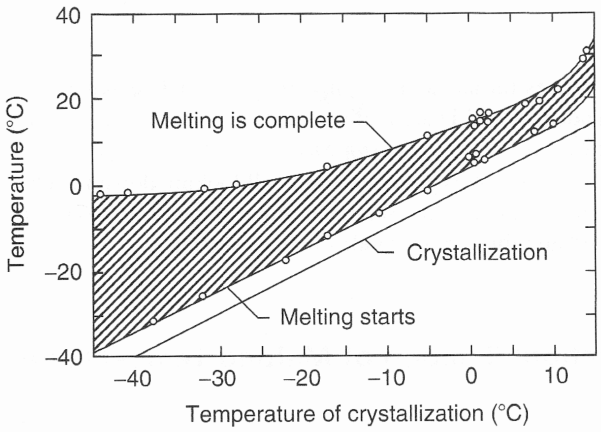


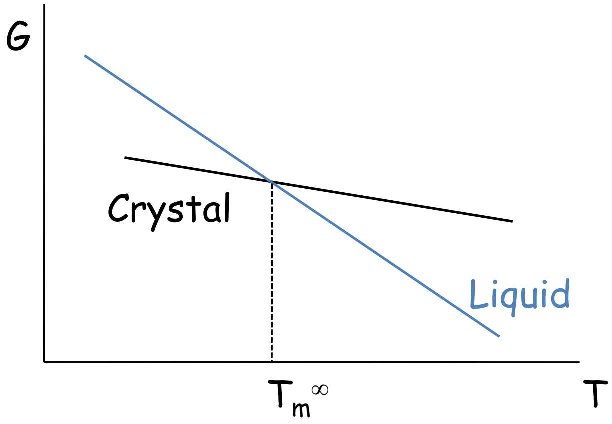
Figure 13.8 Melting temperature of crystals versus temperature of crystallization for *cis* 1,4-polyisoprene. Note the temperature range over which melting occurs. (Reprinted from Wood, L.A. and Bekkedahl, N., *J. Appl. Phys.*, 17, 362, 1946. With permission.)

for polymers M→ ∞

T_m (crystal → liquid)

≠

T_c (liquid → crystal)



Definition of T_m^∞ :
melting point of crystals with infinite dimensions

Thermodynamics of Crystallization

$$\boxed{\text{crystal (c)} \xrightarrow{\text{fusion process (f)}} \text{liquid (l)}}$$

$\Delta G = \Delta H - T\Delta S$

$\Delta G_f = G_l - G_c$

above T_m^∞	$\Delta G_f < 0$	→ melting is spontaneous
below T_m^∞ :	$\Delta G_f > 0$	→ crystallization is spontaneous
at T_m^∞	$\Delta G_f = 0$	→ equilibrium of both phases

$$T_m^\infty = \frac{\Delta H_f}{\Delta S_f}$$

Dependence of T_m on Lamellar Thickness ℓ

for the transition crystal → liquid, ΔG_f is the sum of 2 contribution:

$$\Delta G_f = \Delta G^\infty + \Delta G_s$$

ΔG_s arises specially from surface effects
ΔG^∞ applies to the case of a crystal of infinite size (bulk)
v basis of unit volume
γ Gibbs free energy per unit area of the interface between crystal and surrounding liquid
ΔH_v^∞ heat of fusion

Thompson-Gibbs-Equation:

$$\boxed{\Delta T = 2T_m^\infty \frac{\gamma}{\Delta H_v^\infty} \frac{1}{l}}$$

for r → ∞ (means well developed crystals)

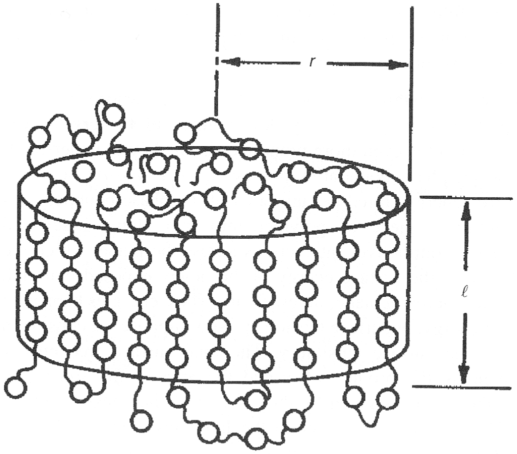


Figure 13.11 Idealized representation of a polymer crystal as a cylinder of radius r and thickness ℓ.

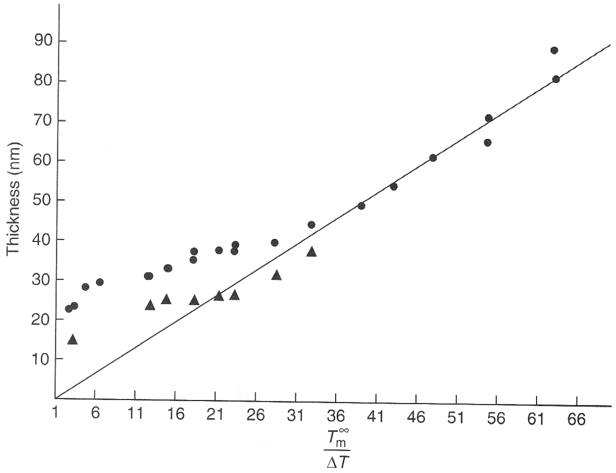


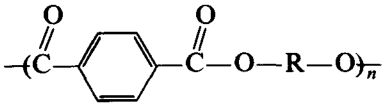
Figure 13.12 Crystal thickness versus $T_m/\Delta T$ for polyethylene. (Reprinted from Mandelkern, L., *Crystallization of Polymers*, McGraw-Hill, New York, 1964. With permission.)

Lamella thickness ℓ depends not on molecular weight, but on undercooling

Effect of Chemical Structure on T_m

Structural irregularities

The effect of structural irregularities can be illustrated by a study of polyesters (152) having the general structure

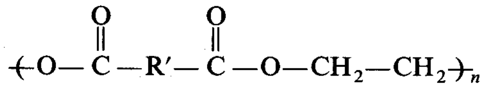


(5.66)

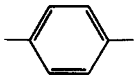
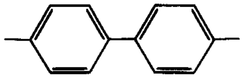
which is the general structure of Dacron. The melting temperature depends on the regularity of the group *R*. For aliphatic groups, the size and regularity of *R* are both important:

R	T_f, °C
$-CH_2-CH_2-$	265
$-(CH_2)_3-$	220
$-CH_2-\underset{\substack{\vert \\ CH_3}}{CH}-$	Noncrystalline

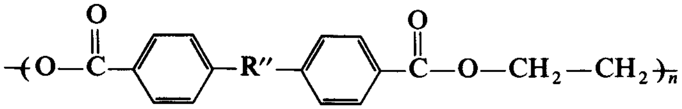
Chain flexibility



$$-\!\!\left(O-\overset{\substack{O\\ \|}}{C}-R'-\overset{\substack{O\\ \|}}{C}-O-CH_2-CH_2\right)_n\!\!-$$

R′	T_f, °C
	265
	355
$-(CH_2)_4-$	50

Interchain forces



R″	T_f, °C
$-(CH_2)_4-$	170
$-O-CH_2-CH_2-O-$	240
$-NH-CH_2-CH_2-NH-$	273

Influence of Molecular Weight on Crystallization

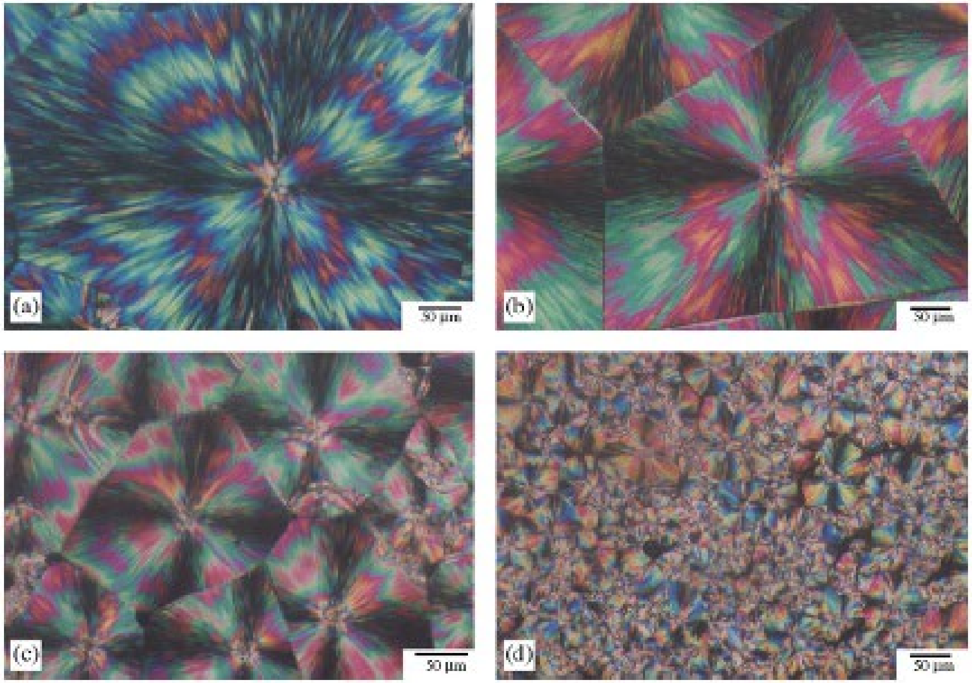


Fig. 11. Morphology in PLM photos for PTTs with different molecular weight isothermally crystallization at 190 °C for 30 min from the melt state. PTT-1 ($M_\eta = 12800$); PTT-2 ($M_\eta = 17600$); PTT-3 ($M_\eta = 21200$); PTT-4 ($M_\eta = 28000$).

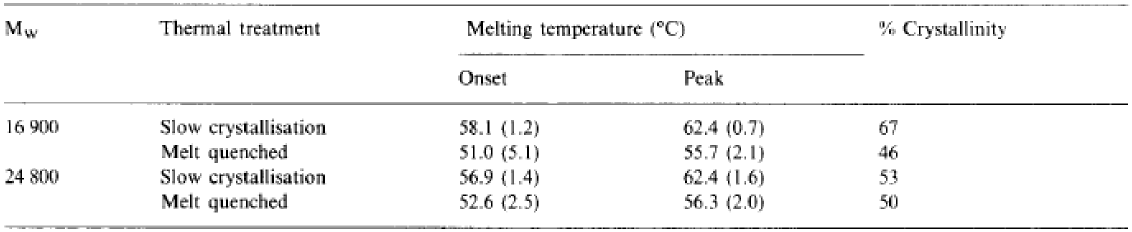
PPT polytrimethylene terephthalate

$$\boxed{\frac{1}{T_m} - \frac{1}{T_m^{\infty}} = \frac{R}{\Delta H_f} \frac{2M_0}{M_n}}$$

T_m melting point under consideration
T_m^{∞} melting point of the polymer of infinite MW
M_0 molecular weight of repeat unit

Kinetics matters !

Table 3
Thermal properties of PCL (mean with 95% C.I.)



M_W	Thermal treatment	Melting temperature (°C)		% Crystallinity
		Onset	Peak	
16 900	Slow crystallisation	58.1 (1.2)	62.4 (0.7)	67
	Melt quenched	51.0 (5.1)	55.7 (2.1)	46
24 800	Slow crystallisation	56.9 (1.4)	62.4 (1.6)	53
	Melt quenched	52.6 (2.5)	56.3 (2.0)	50

Lit.: L. Mandelkern, Biophysical Chem. 112 (2004), 109-116.
PCL: polycaprolactone

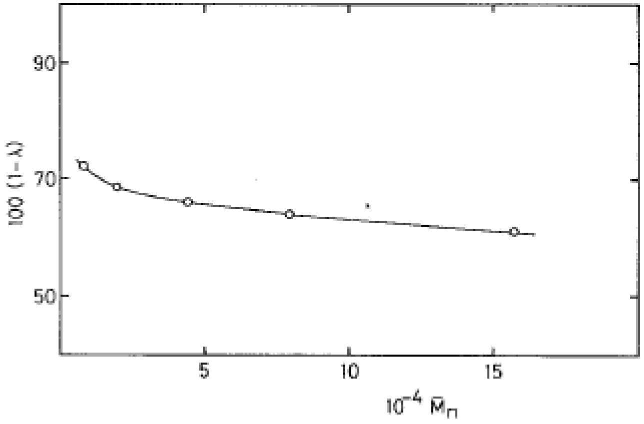


Fig. 3. Degree of crystallinity against molecular weight

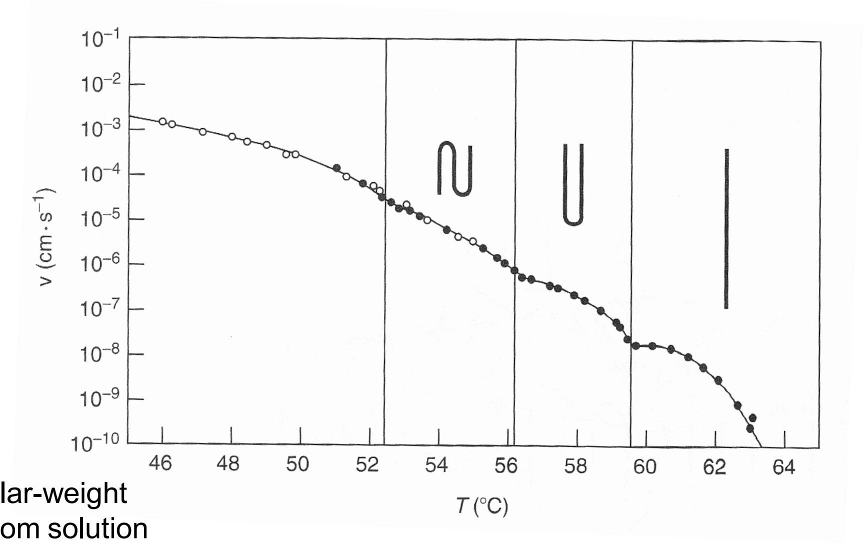
Kinetic of Crystallization

Crystallization = Nucleation and Growth

Nucleation: appearance of domains of the new phase that are sufficiently large to become stable

- heterogeneous: a foreign particle or surface provides a site for facile nucleation
- homogeneous: spontaneous formation of nuclei by random fluctuations

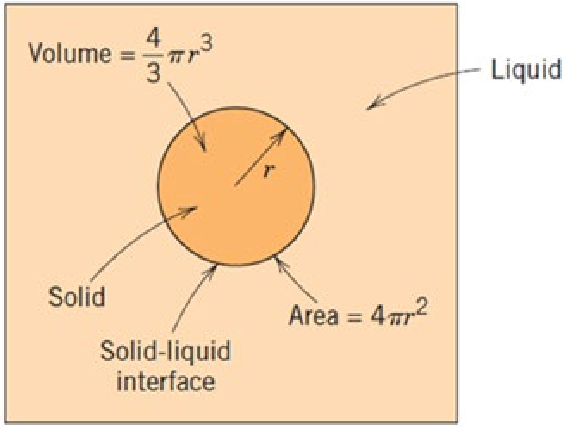
Growth: growth of the phase by adding polymer chains



Crystal growth rate for low molecular-weight poly(ethylene oxide) crystallized from solution

Nucleation

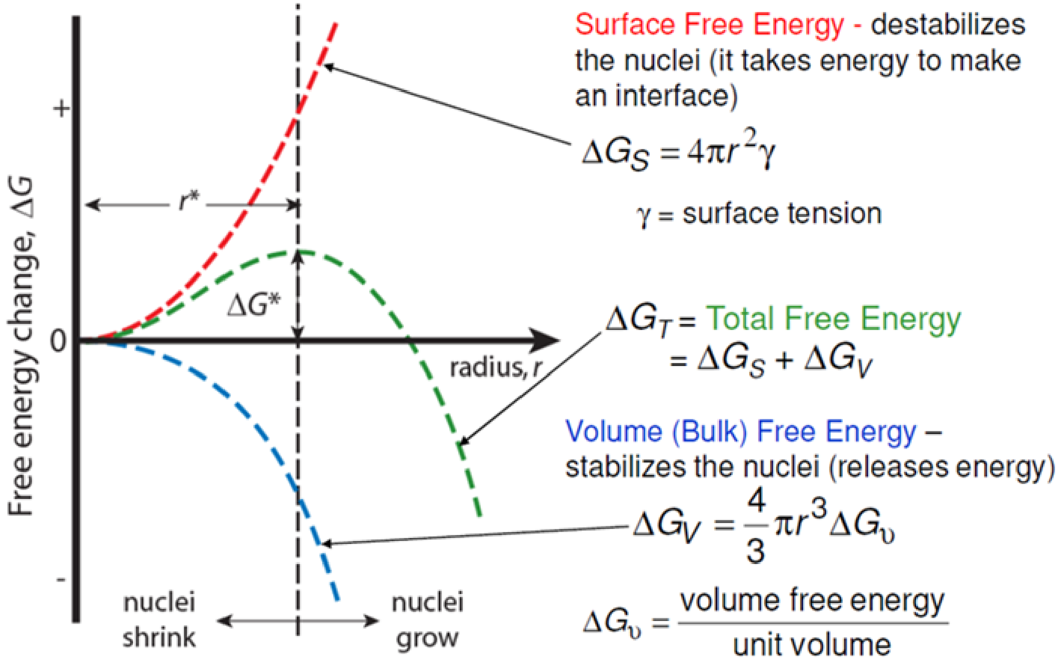
ΔG of a spherical droplet with radius R of the new phase is the sum of a surface term and a volume term



$$\boxed{\Delta G(R) = 4\pi R^2\,\gamma\ + \frac{4\pi}{3}R^3\Delta G_v}$$

with γ = surface energy

Nucleation



Surface Free Energy - destabilizes the nuclei (it takes energy to make an interface)

$\Delta G_S = 4\pi r^2 \gamma$

γ = surface tension

ΔG_T = Total Free Energy $= \Delta G_S + \Delta G_V$

Volume (Bulk) Free Energy – stabilizes the nuclei (releases energy)

$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$

$\Delta G_\upsilon = \frac{\text{volume free energy}}{\text{unit volume}}$

r^* = critical nucleus: for $r < r^*$ nuclei shrink; for $r > r^*$ nuclei grow (to reduce energy)

Critical Nucleus with R*: $R^* = -2\gamma/\Delta G_v$ with a free-energy barrier given by $\Delta G^* = (16\pi/3)(\gamma^3/\Delta G_v^2)$

→The critical nucleus shrinks as the crystallization temperature decreases, so nuclei are easier to form

→The nucleation barrier height depends on the inverse square of the undercooling, so nucleation should be more facile at lower temperature

Nucleation

Critical nucleus size is on the order of 10 nm

→ what sets the thickness of the crystal nucleus?

Critical stem length l*; $l^* = -4\gamma/\Delta G_v$

→l* depends on the inverse undercooling → thicker nuclei as T_c is lowered

The critical barrier height: $\Delta G(p^*,l^*) = 8\pi\gamma^3/\Delta G_v^2$ p* = critical number of stems

stem = section of chain that traverses a lamella

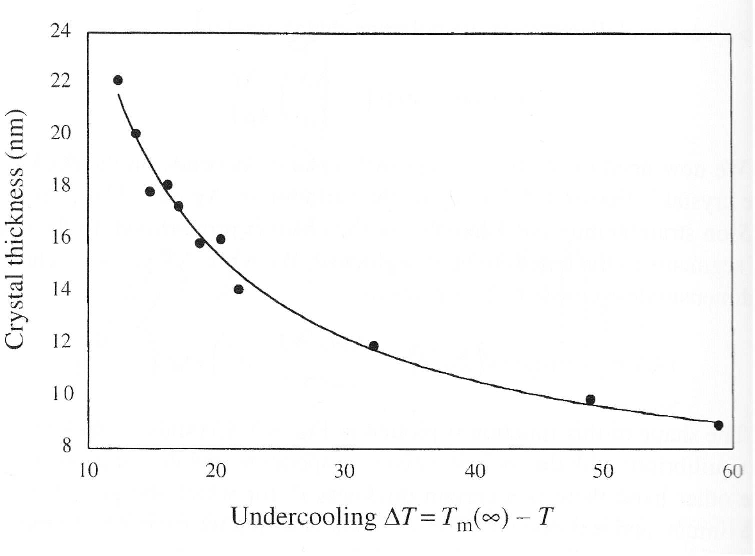


Fig. 8.6 Crystal thickness as a function of undercooling for polyethylene, showing good agreement with the functional form of eqn 8.7. Data from Barham *et al.* (1985).

Growth

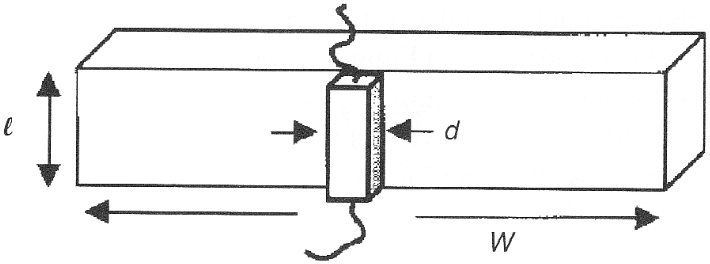


Figure 13.19 Schematic of the secondary nucleation process, whereby a single complete new stem adds to a perfectly flat crystal face.

overall growth velocity $v = dWr_s$ [length^{-1} time^{-1}]

overall rate of secondary nucleation: $r_s \propto \exp\left(-\dfrac{B}{T - T_0}\right) \exp\left(-\dfrac{\Delta G_s^*}{kT}\right)$

Once the secondary nucleus is in place, the rest of the layer could fill in by adding adjacent stems. Each new stem increases the crystal volume by the same amount, d^2l, but also increases the fold surface area by $2d^2$.

Kinetics of Bulk Crystallization -Avrami-Equation-

Combination of the rates of nucleation and growth give the net rate of crystallization

Model: - crystals are circular disks lying in the same plane
- nucleation is assumed to begin simultaneously from centers positioned at random throughout the liquid
- growth in the radial direction at a constant velocity

Avrami-Equation

$$\boxed{\phi_c = 1 - \exp(-Kt^m)}$$

m = Avrami exponent
K = associated rate constant
ϕ_c = crystalline fraction
1 - ϕ_c = amorphous fraction

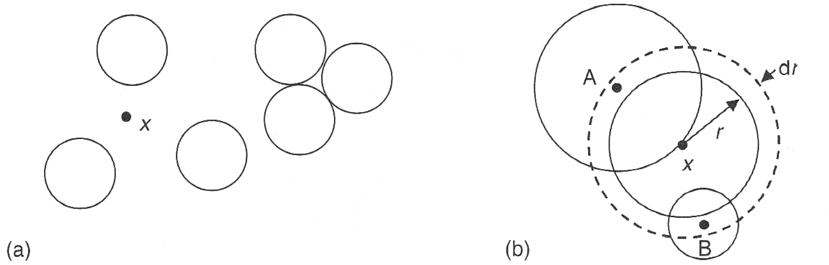


Figure 13.30 The growth of disk-shaped crystals. (a) All crystals have been nucleated simultaneously. All crystals have the same radius $\dot{r}t$ after an elapsed time t. (b) Nucleation is sporadic. Crystal A has had enough time to reach point x, while B has not, although both originate in the same ring a distance r from x.

Avrami Exponents andTest of Avrami Equation

Summary of Exponents in the Avrami Equation for Different Crystallization Mechanisms

Avrami exponent	Crystal geometry	Nucleation mode	Rate determination
0.5	Rod	Simultaneous	Diffusion
1	Rod	Simultaneous	Contact
1	Disk	Simultaneous	Diffusion
1.5	Sphere	Simultaneous	Diffusion
1.5	Rod	Sporadic	Diffusion
2	Disk	Simultaneous	Contact
2	Disk	Sporadic	Diffusion
2	Rod	Sporadic	Contact
2.5	Sphere	Sporadic	Diffusion
3	Sphere	Simultaneous	Contact
3	Disk	Sporadic	Contact
4	Sphere	Sporadic	Contact

$$\ln\left[\ln\left(\frac{1}{1-\phi_c}\right)\right] = m\ lnt + lnK$$

Table 6.4 The Avrami parameters for crystallization of polymers (83)

	Crystallization Mechanism	Avrami Constants Z	n	Restrictions
Spheres	Sporadic	$2/3\pi g^3 l$	4.0	3 dimensions
	Predetermined	$4/3\pi g^3 L$	3.0	3 dimensions
Discs[a]	Sporadic	$\pi/3g^2 ld$	3.0	2 dimensions
	Predetermined	$\pi g^3 Ld$	2.0	2 dimensions
Rods[b]	Sporadic	$\pi/4gld^2$	2.0	1 dimension
	Predetermined	$\frac{1}{2}\pi gLd^2$	1.0	1 dimension

[a] Constant thickness d.

[b] Constant radius d.

Z = K and n = m

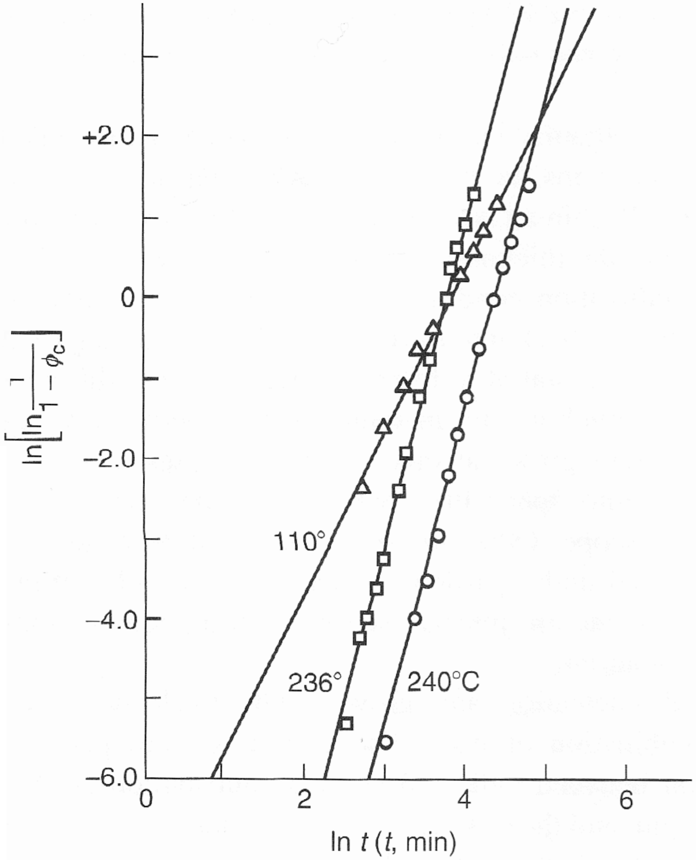


Figure 13.34 Log–log plot of $\ln(1-\phi_c)^{-1}$ versus time for poly(ethylene terephthalate) at three different temperatures. (Reprinted from Morgan, L.B., *Philos. Trans. R. Soc. London*, 247A, 13, 1954. With permission.)

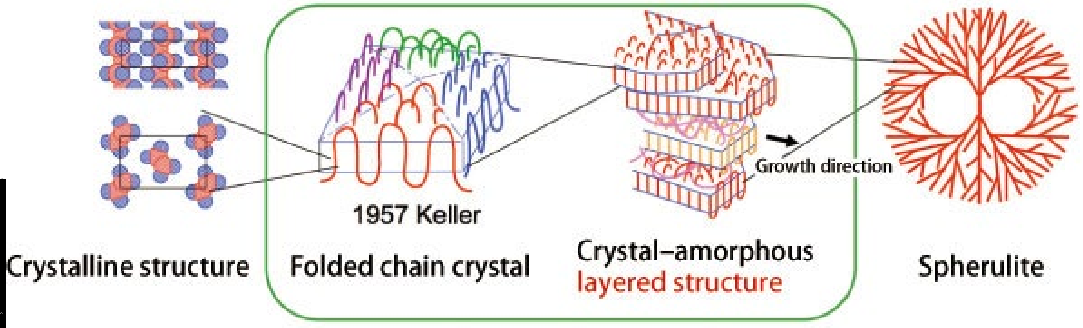
Summary of Crystallization Kinetics

Polymer crystals emerge by a process of nucleation and growth. The nucleation may be heterogeneous, homogeneous or a combination of both. The barrier to homogeneous nucleation is dependent on the competition between bulk and surface contributions to the free energy; in general nucleation is more rapid, and the critical nuclei size smaller, the greater the undercooling.

The growth process at the level of an individual lamella is still not fully understood, but in many cases the temperature dependence of the growth rate can be interpreted via the competition between the rate of addition of a single stem to a growth face and the rate of adding stems at neighboring sides.

The overall evolution of crystallinity often follows the Avrami equation, in which the type of nucleation, the spatial dimensionality of growth, and the presence or absence of diffusion limitations interact to yield a particular Avrami exponent. At relatively small undercoolings the rate of crystallization increases as temperature decreases, but eventually the rate decreases and vanishes as the approach to the glass transition inhibits any kind of chain or segmental motion. The overall rate of crystallization is typically independent of molecular weight for high-molecular weight polymers, but increases with decreasing molecular weight for shorter chains.

Crystallization of Polymers from the Melt



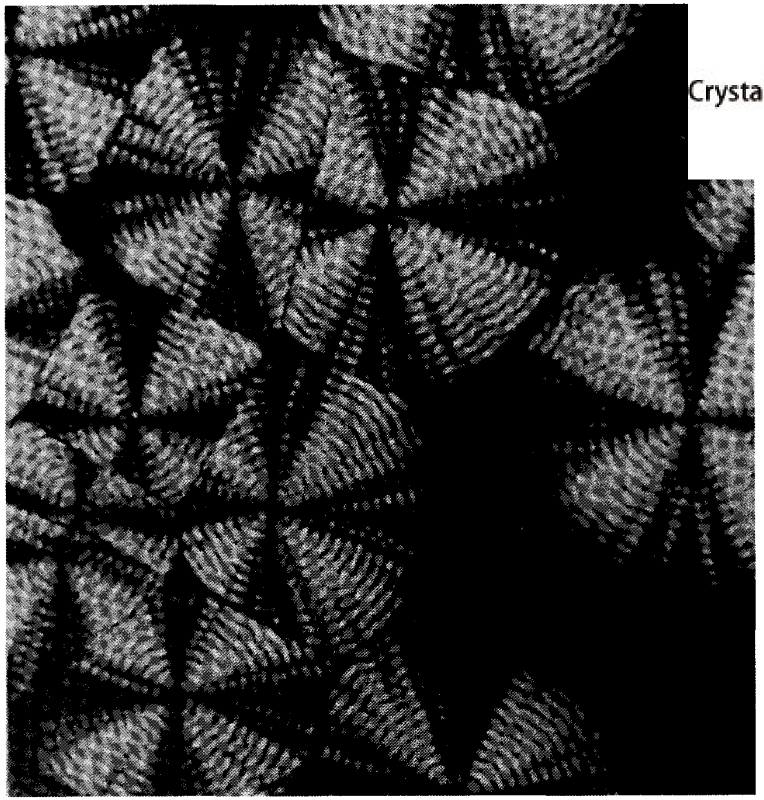


Figure 4.12 Spherulites of poly(1-propylene oxide) observed through crossed Polaroid filters by optical microscopy. See text for significance of Maltese cross and banding in these images. [From J. H. MaGill, *Treatise on Materials Science and Technology*, Vol. 10A, J. M. Schultz (Ed.), Academic, New York, 1977, with permission.]

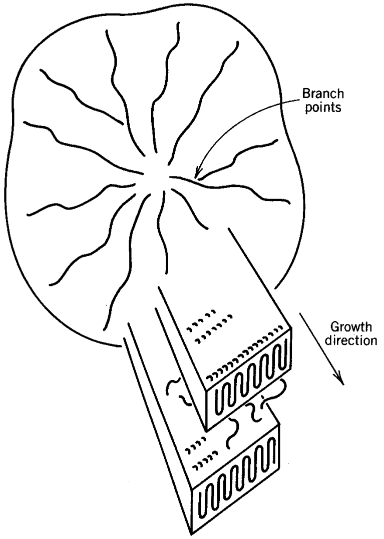


FIGURE 5.26 Model of spherulitic structure. Note growth directions and lamellar branch points, so to fill space uniforming with crystalline material. After J. D. Hoffman, G. T. Davis, and J. I. Lauritzen, Jr. (77).

Crystallization of Polymers from Dilute Solution

Rapidly stirring or spinning of fibers from dilute solutions results in:

Nonspherulitic Morphologies: Shish Kebabs

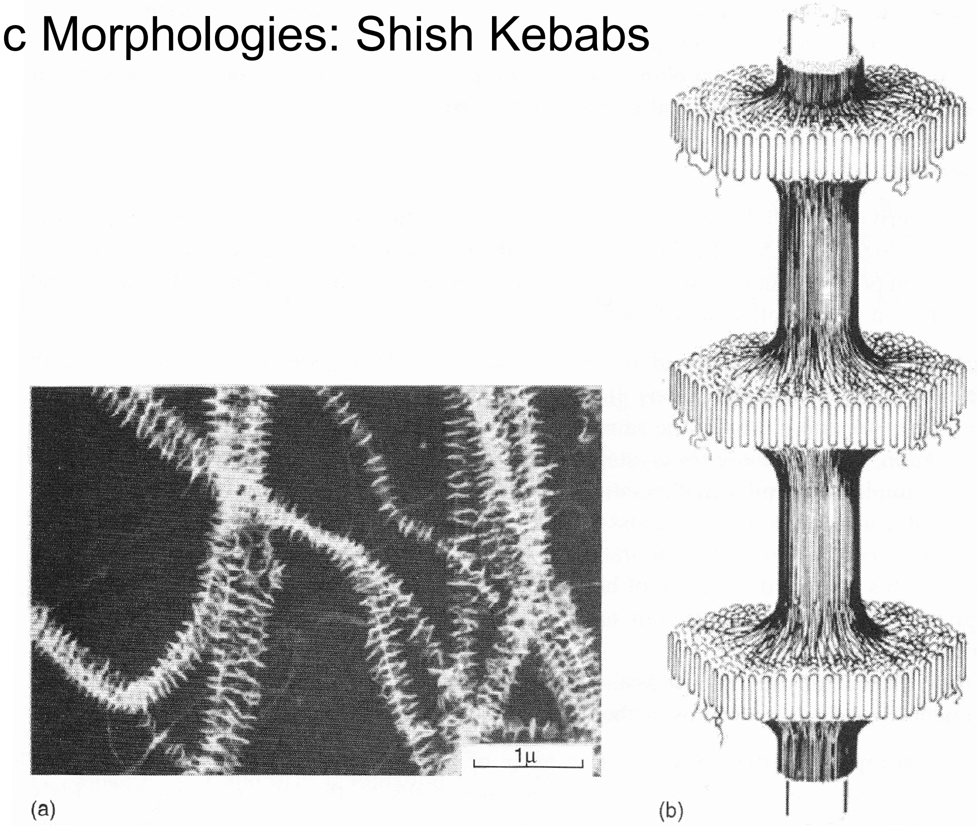
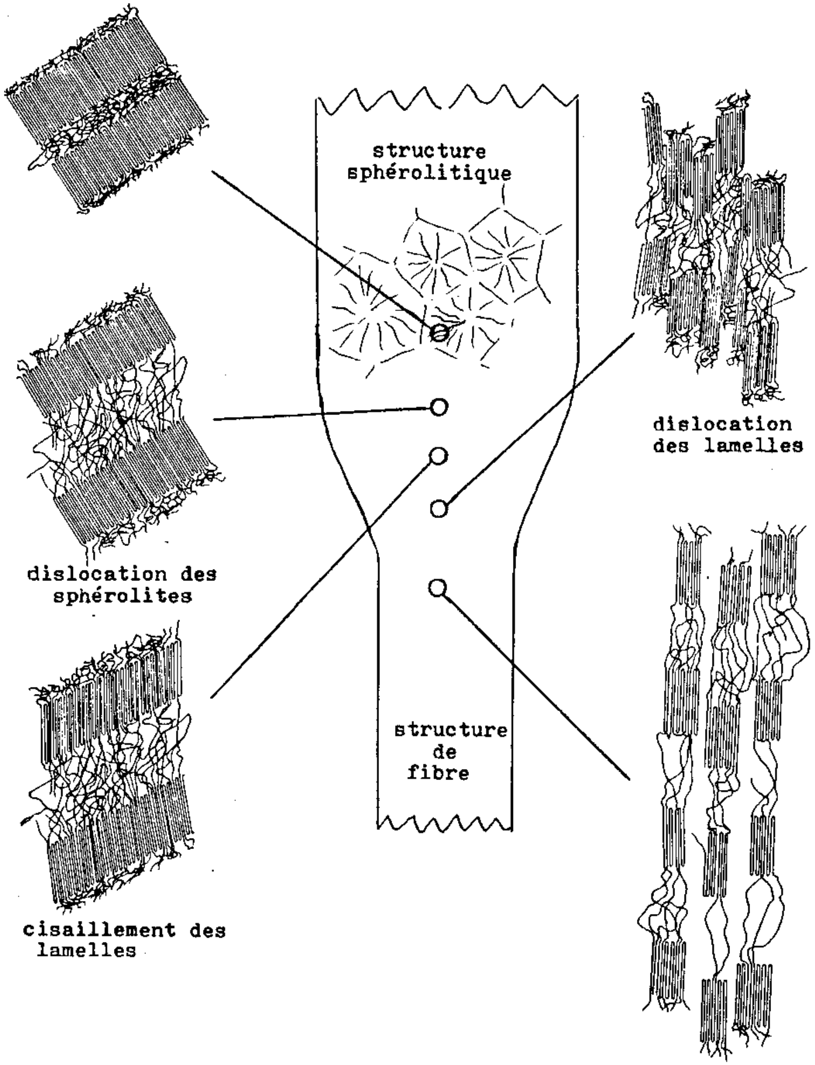
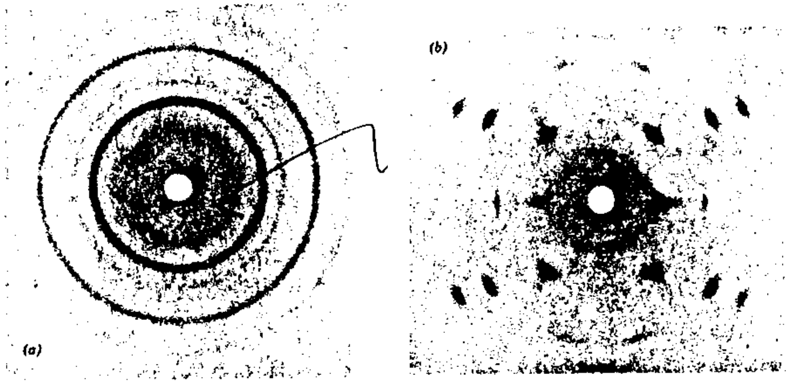
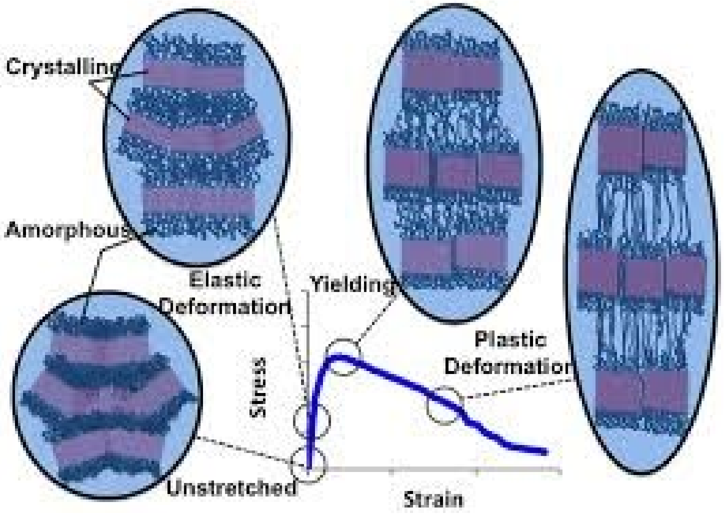


Figure 13.29 Transmission electron micrograph of polyethylene shish kebabs crystallized from xylene solution during flow (a), and (b) schematic of the underlying chain structure. (Reproduced from Pennings, A.J., van der Mark, J.M.A.A., and Kiel, A.M., *Kolloid Z.Z. Polym.*, 237, 336, 1970. With permission.)

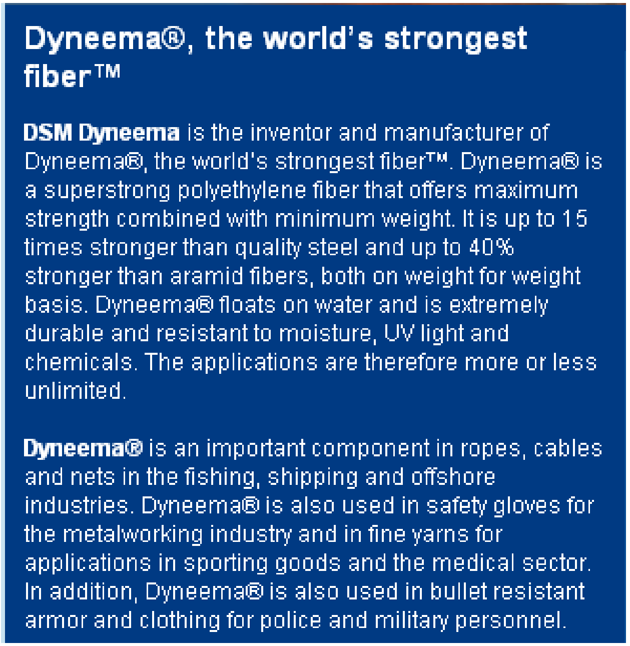
Fibers: Strain Induced Orientation of Crystallites







Ultrastrong Polymer Fibers



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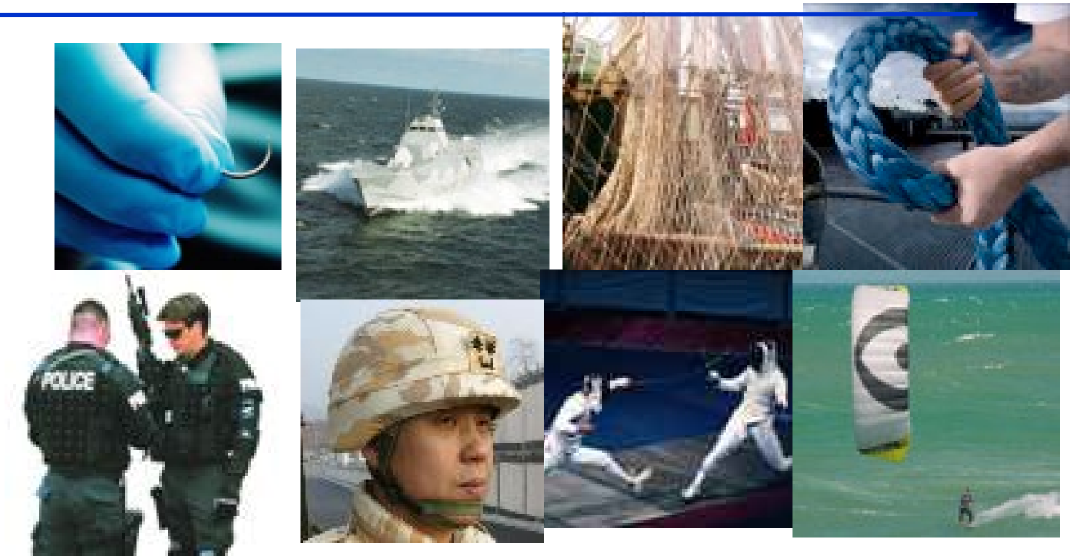

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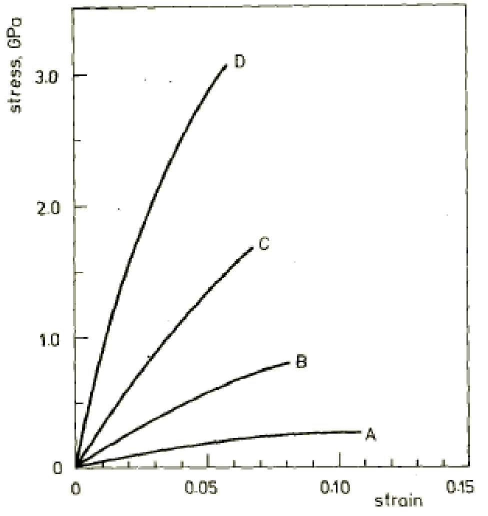

Figure 5 Stress–strain curves of solution-spun/drawn polyethylene fibres. Draw ratios: A 2.8; B 8.4; C 15.7; D 31.7.

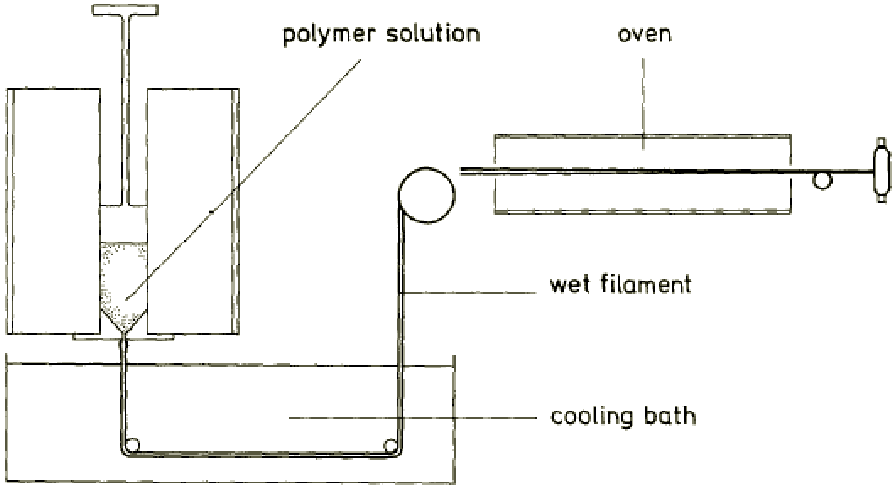

Figure 1 Schematic representation of the solution spinning/drawing process.

P. Smith, P. J. Lemstra, *J. Mat. Sci.* **1980**, *15*, 505

Summary

1. At the smallest structural length scale, the unit cell, individual chains form helices to minimize intramolecular energetic constraints, and the helices pack together to maximize intermolecular interactions. Polymer unit cells represent many of the 230 possible space groups, except those with cubic symmetry, and it is not unusual for a given polymer to exhibit two or more different polymorphs under different conditions.

2. On intermediate length scale the unit cells are organized into chain-folded lamellae, such that portions of the individual chain backbones, or stems, lie parallel to each other and approximately parallel to the thin axis of the lamella. Within an isothermally crystallized sample, the lamellae are of roughly constant thickness, but the thickness varies from a few tens to a few hundreds of angstroms, depending on crystallization conditions. Upon exiting lamellar surface, a particular chain may execute a tight fold back into the crystal to become an adjacent stem, or it may wander off to reenter the same crystal at a different site, or even a different lamella. The prevalence of adjacent reentry is much grater in solution-grown single crystals than in melt-crystallized materials, and in crystals grown at smaller undercoolings.

3. On larger scales the lamellae grow into spherulites, which may be viewed and characterized with a polarizing optical microscope. Other morphologies such as dendrites, hedrites, and shish kebab can also be observed under particular conditions. A bulk sample never becomes 100% crystalline, and the lamellae are interspersed with amorphous regions that can often comprise the majority of the material.